SELENIUM COMPOUNDS

Selenium compounds are federal hazardous air pollutants and were identified as toxic air contaminants in April 1993 under AB 2728.

CAS Registry Number of Selenium: 7782-49-2 Se

Selenium monosulfide: 7446-34-6 SeS

Molecular Formula of Selenium: Se

Selenium monosulfide: SSe

Elemental selenium exists in several allotropic forms. The amorphous form is either red in powder form, or black in vitreous form. The crystalline monoclinic prism form is deep red and the black crystalline hexagonal form (the most stable variety) is a lustrous metallic gray. Selenium is odorless and insoluble in water and alcohol, but soluble in chloroform, methylene iodide, benzene, quinoline, nitric acid, sulfuric acid, ether, carbon disulfide, aqueous potassium cyanide and potassium sulfate solutions (HSDB, 1991; Sax, 1989). Selenium possesses photovoltaic (converts radiant energy to electrical energy) and photoconductive (where electrical resistance decreases with increased illumination) properties. There are six isotopes (Merck, 1989).

The properties of selenium compounds vary with the individual selenium compound. Selenium sulfide is the only selenium compound currently shown to be carcinogenic in animals. It is a bright orange powder which emits toxic fumes of selenium and sulfur oxides when heated to decomposition (Sax, 1989). It is soluble in benzene and carbon disulfide.

Examples of Selenium Compounds

Selenic acid	Selenium dioxide	Selenourea
Seleninyl bis(dimethylamide)	Selenium hexafluoride	Selsun
Seleninyl bromide	Selenium monosulfide	Sodium selenite
Selenious acid	Selenium tetrachloride	Sodium selenate
Selenium (colloidal)	2-Selenoethylguanidine	Selenium disulfide
Selenium anhydride	6-Selenoguanosine	Selenium monochloride
Selenium trioxide	Selenomethionine	Selenium oxychloride
Selenium dimethyldithiocarbamate		-

Physical Properties of Selenium and Selenium Monosulfide

Synonyms for selenium: CI 77805

Synonyms for selenium monosulfide: selenium sulfide; selensulfid; sulfur selenide

	<u>Selenium</u>	Selenium Monosulfide
Atomic Number:	34	
Valences:	2,4,6	
Molecular Weight:	78.96	111.02
Boiling Point:	690 °C	118 °C
Melting Point:	170 - 217 °C	< 100 °C
Density/Specific Gravity:	4.26	3.056 at °C
Vapor Pressure:	$0.001 \text{ mm Hg at } 20 ^{\circ}\text{C}$	

(Merck, 1989; Sax, 1989; U.S. EPA, 1994a)

SOURCES AND EMISSIONS

A. Sources

Selenium is used in the glass industry as a decolorizing agent and as a pigment. It is also used in the production of electrodes for arc lights, electrical instruments, selenium photocells, semiconductor fusion mixtures, photographic emulsions, as a vulcanizing agent in the processing of rubber, in the manufacture of metal alloys, and as a trace element in animal feed (Merck, 1989; Sax, 1987). The primary stationary sources that have reported emissions of selenium in California are glass manufacturing facilities, and petroleum refining sites (ARB, 1995a).

Selenium sulfides are used as pharmaceutical and veterinary drugs to topically treat eczemas and dermatomycoses. They are also used as external preparations in shampoos for dandruff and for control of sebhorrheic dermatitis and nonspecific dermatoses (Merck, 1989; Goodman and Gilman, 1985). The primary stationary sources that have reported emissions of selenium sulfide in California are metal mining sites, and for selenium and other selenium compounds the primary stationary sources that have reported emissions in California are electrical services, and manufacturers of flat glass, and of pressed or blown glass (ARB, 1997b).

B. Emissions

The total emissions of selenium, selenium sulfide, and other selenium compounds from stationary sources in California are estimated to be at least 19,000 pounds per year, based on data reported under the Air Toxics "Hot Spots" Program (AB 2588). Of the 19,000 pounds of emissions, at least 13,000 pounds were contributed by selenium, at least 4,800 pounds were contributed by selenium sulfide, and at least 400 pounds were contributed by other selenium compounds (ARB, 1997b).

C. Natural Occurrence

Selenium constitutes about 0.09 parts per million of the earth's crust and appears in the sulfide ores of heavy metals and is found in pyrite, clausthalite, naumannite, tiemannite and in selenosulfur (Merck, 1989). Coal and soils surrounding volcanos tend to have higher amounts of selenium. Selenium is released to the atmosphere as selenious acid and elemental selenium with the combustion of fossil fuels (HSDB, 1991).

AMBIENT CONCENTRATIONS

Selenium and its species are routinely monitored by the statewide Air Resources Board air toxics network. The network's mean concentration of selenium (including its species) from January 1996 through December 1996 is estimated to be 1.6 nanograms per cubic meter (ng/m³) (ARB, 1997c).

The atmospheric level of selenium in most urban regions ranges from 0.1 to 10 ng/m^3 . A greater part of the atmospheric selenium is bound to fly ash and to suspended particles that contain from 1.4 to 11 micrograms per gram (μ g/g) and from 1 to 110μ g/g, respectively. Up to 90% of the selenium content in ambient air is emitted during the burning of fossil fuels. Selenium dioxide is formed during combustion of elemental selenium present in fossil fuels (HSDB, 1991).

INDOOR SOURCES AND CONCENTRATIONS

In a field study conducted in southern California, investigators collected particles (PM₁₀) inside 178 homes and analyzed the particle samples for selected elements, including selenium. Two consecutive 12-hour samples were collected inside and immediately outside each home. Selenium was present in measurable amounts in less that 10 percent of the samples (Clayton et al., 1993).

ATMOSPHERIC PERSISTENCE

Dimethyl selenide and dimethyl diselenide exist in the atmosphere in the vapor phase, while other selenium compounds exist in the atmosphere in the particulate phase (elemental selenium may also exist in the gas phase in the atmosphere) (Mosher and Duce, 1989). The average half-life and lifetime for particles and particle-associated chemicals in the troposphere is about 3.5 to 10 days and 5 to 15 days, respectively. Dimethyl selenide has a short atmospheric half-life and lifetime due to gas-phase reaction with hydroxyl radicals, nitrate (NO₃) radicals, and O₃, of a few hours or less (Atkinson et al., 1990).

AB 2588 RISK ASSESSMENT INFORMATION

The Office of Environmental Health Hazard Assessment reviews risk assessments submitted under the Air Toxics "Hot Spots" Program (AB 2588). Of the risk assessments reviewed as of April 1996, selenium and selenium compounds contributed to the total cancer risk in 101 of the approximately 550 risk assessments reporting a total cancer risk equal to or greater than 1 in 1 million. Selenium and selenium compounds also contributed to the total cancer risk in 34 of the approximately 130 risk assessments reporting a total cancer risk equal to or greater than 10 in 1 million (OEHHA, 1996a).

For the non-cancer health effects, selenium and selenium compounds contributed to the total hazard index in 19 of the approximately 89 risk assessments reporting a total chronic hazard index greater than 1. Selenium and selenium compounds also contributed to the total hazard index in 40 of the approximately 107 risk assessments reporting a total acute hazard index greater than 1, and presented an individual hazard index greater than 1 in 6 of these risk assessments (OEHHA, 1996b).

HEALTH EFFECTS

Probable routes of human exposure to selenium and selenium compounds are inhalation, ingestion, and dermal contact (NTP, 1994).

Non-Cancer: Selenium is a nutritionally essential element. Overexposure to selenium and its compounds may cause eye, skin, and respiratory tract irritation and may also cause pulmonary edema. Selenium is a general cellular poison. Chronic intoxication may cause depression, nervousness, dermatitis, gastrointestinal upset, metallic taste in mouth and garlicky odor of breath, increased dental caries, and loss of fingernails or hair. The liver and kidneys are also target organs. People with a history of dermatitis, chronic bronchitis, skin allergy or respiratory tract infection, history of liver or kidney disease, jaundice or albuminuria and women during their childbearing period may be more sensitive to the effects of selenium (HSDB, 1991; Sittig, 1991).

An acute Reference Exposure Level (REL) of 2 micrograms per cubic meter (μ g/m³) is listed in the California Air Pollution Control Officers Association (CAPCOA) Revised 1992 Risk Assessment Guidelines for selenium, based on respiratory irritation. The CAPCOA has also listed a chronic non-cancer REL of $0.5~\mu$ g/m³ for selenium compounds. The toxicological endpoint considered for chronic toxicity is the respiratory system (CAPCOA, 1993). The United States Environmental Protection Agency (U.S. EPA) has established an oral Reference Dose (RfD) of 0.005 milligram per kilogram per day for selenium based on clinical selenosis in humans. The U.S. EPA estimates that consumption of this dose or less, over a lifetime, would not likely result in the occurrence of chronic, non-cancer effects. The U.S. EPA has not established a Reference Concentration (RfC) (U.S. EPA, 1994a).

No information is available on adverse developmental or reproductive effects of selenium in humans. Consumption of high levels of selenium by pig, sheep, and cattle has been shown to interfere with normal fetal development and produce fetal malformations (U.S. EPA, 1994a).

Cancer: The only selenium compound that has been shown to be carcinogenic in animals is selenium monosulfide, which has resulted in an increase in liver tumors from oral exposure. The U.S. EPA has placed selenium in Group D: Not classifiable as a carcinogen; and selenium sulfide in Group B2: Probable human carcinogen (U.S. EPA, 1994a). The International Agency for Research on Cancer has placed selenium and selenium compounds in Group 3: Not classifiable as carcinogens (IARC, 1987a).

The State of California under Proposition 65 has determined that selenium sulfide is a carcinogen (CCR, 1996). The preliminary recommended potency value for use in cancer risk assessments is 1.4×10^{-4} (microgram per cubic meter)⁻¹. In other words, the potential excess cancer risk for a person exposed over a lifetime to $1 \mu g/m^3$ of selenium sulfide is estimated to be no greater than 140 in 1 million (CAPCOA, 1993).